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ACTIVE MATERIAL FOR BATTERY AND METHOD OF PREPARING SAME

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to an active material for a battery and a method of preparing the same, and more particularly, to an active material for a battery with excellent electrochemical characteristics and thermal stability, and a method of preparing the same.

(b) Description of the Related Art

In recent times, pursuant to reductions in size and weight of portable electronic equipment, there has been a need for developing batteries for such portable equipment with high energy density and high power density. Furthermore, it is required that such batteries be produced in a cost effective manner while being reliable and safe.

Batteries are usually classified as primary batteries that can be used only once and then disposed of, and secondary batteries that can be recharged and used repeatedly. Primary batteries include manganese batteries, alkaline batteries, mercury batteries, and silver oxide batteries. Secondary batteries include lead-acid storage batteries, nickel-metal hydride (Ni-MH) batteries, sealed nickel-cadmium batteries, lithium metal batteries, lithium ion batteries, lithium polymer batteries, and lithium-sulfur batteries.

Such batteries generate electric power through using an electrochemical reaction material (referred to hereinafter simply as the “active

material") for a positive electrode and a negative electrode. Critical factors for determining battery capacity, safety and reliability are electrochemical characteristics and thermal stability of the active material, and extensive research has been made to improve such factors.

Of currently available active materials, lithium metal involves high energy density per unit volume and high electronegativity, and hence it can be well adapted for use in producing high voltage battery cells. However, lithium metal also involves safety problems when it is used alone. Accordingly, it has been widely proposed that a material capable of intercalating or deintercalating lithium metal or ions might be used for the active material.

For instance, a rechargeable lithium battery cell generates electric energy by way of oxidation and reduction reactions (called "redox") occurring when the lithium ions are intercalated and deintercalated at the positive and negative electrodes. In a rechargeable lithium battery cell, a material having a structure where lithium ions can be reversibly intercalated and deintercalated during charge and discharge is used for the positive and negative electrodes, and an organic electrolyte or a polymer electrolyte is filled between the positive and the negative electrodes.

Lithium metal has been used as the negative active material. However, with the use of lithium metal, dendrites may be formed within the battery cell, causing short circuits and explosion of the battery cell. Therefore, a carbon-based material such as amorphous carbon or crystalline carbon has replaced metallic lithium. Particularly, boron-coated graphite (BOC), where boron is added to the carbon-based material, has recently been spotlighted as a high

capacity negative active material.

It has been proposed that lithium metal oxides such as $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, $LiNi_{1-x}Co_xO_2$ ($0<x<1$) and $LiMnO_2$, or chalcogenide compounds might be used as the positive active material for the lithium secondary battery. Manganese-based positive active materials such as $LiMn_2O_4$ and $LiMnO_2$ can be easily synthesized at a low cost while contributing little to environmental pollution. However, such a manganese-based positive active material bears a low capacity. $LiCoO_2$ is currently the most popular material for the positive electrodes of commercially available lithium secondary battery. This compound has high electrical conductivity, high cell voltage and excellent electrode characteristics, but it involves high production costs. Among the above positive active materials, $LiNiO_2$ involves the lowest cost while bearing the highest discharge capacity, but it cannot be easily synthesized.

95% of the batteries that are circulated throughout the world use the $LiCoO_2$-based positive active material, and there have been continual attempts to replace this high-cost active material with a new one. Rechargeable lithium batteries using a powder of $LiCoO_2$ for the positive electrode exhibit relatively long shelf life and an excellent discharge profile, but there is also a need to make consistent capacity improvements to such batteries.

In order to improve the $LiCoO_2$-based positive active material, research has been carried out on the substitution of metal oxide for a part of the Co. The Sony corporation developed a powder of $LiCo_{1-x}Al_xO_2$ where Al_2O_3 is doped at about 1 to 5 wt% and Al is substituted for part of the Co, and applied it for use in mass production. The A&TB (Asahi & Toshiba Battery Co.) company

developed a positive active material where SnO_2 is doped, and Sn is substituted for part of the Co.

U.S. Patent No. 5,292,601 discloses Li_xMO_2 where M is one or more elements selected from Co, Ni or Mn, and x is 0.5 to 1, as an improved active material over $LiCoO_2$. U.S. Patent No. 5,705,291 discloses a technique where a material selected from boron oxide, boric acid, lithium hydroxide, aluminum oxide, lithium aluminate, lithium metaborate, silicon dioxide, lithium silicate or mixtures thereof is mixed with a lithiated intercalation compound, and the mixture is baked at 400℃ or more such that the oxide content is coated onto the surface of the lithiated intercalation compound.

Japanese Patent Laid-Open No. 9-55210 discloses a positive active material prepared through coating an alkoxide of Co, Al and Mn on the lithium-nickel based oxide, and heat-treating the alkoxide-coated oxide. Japanese Patent Laid-Open No. 11-16566 discloses a lithium-based oxide material coated with metal selected from Ti, Sn, Bi, Cu, Si, Ga, W, Zr, B or Mo, and/or an oxide thereof. Japanese Patent Laid-Open No. 11-185758 discloses a positive active material where metal oxide is coated onto lithium manganese oxide through dipping, and heat treatment is performed thereto.

As shown in Fig. 1, the currently available positive electrode is fabricated through dry-mixing an active material with a conductive agent, adding the mixture to a binder-containing solution to prepare a slurry, and coating the slurry onto a current collector and pressing it to thereby form an electrode. The conductive agent has a large surface area of $2500m^2/g$ or more, and hence it causes an increase in the thickness of the electrode. Furthermore, the

amount of active material is decreased by the amount of a conductive agent added, and this works as a hindrance to the fabrication of a high capacity battery.

In order to solve such a problem, it has been proposed that the amount of the conductive agent and the binder should be decreased. However, such a technique cannot well serve to improve the electrochemical characteristics of the battery.

In the above description, positive active materials of lithium secondary batteries and related examples of developments were explained. Recently, in relation to the tendency to develop portable electronic equipment that is more compact and lightweight, other types of batteries have the same demands for an active material that guarantees battery performance, safety and reliability. Research and development is therefore accelerated on electrochemical properties and thermal stability of positive active materials to ensure improved performance, safety and reliability of batteries.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an active material for a battery which bears excellent electrochemical characteristics and thermal stability.

It is another object of the present invention to provide a method of preparing an active material for a battery in a cost-effective manner while involving high production efficiency.

It is still another object of the present invention to provide a high density

electrode for a battery.

It is still another object of the present invention to provide a battery which exhibits excellence in cell capacity and safety.

These and other objects may be achieved by an active material for a battery with a coating layer comprising a conductive agent, or a coating layer comprising a mixture of a conductive agent and a conductive polymeric dispersant.

According to one aspect of the present invention, the active material is prepared through the steps of: (a) preparing a coating liquid where a conductive agent, a dispersant and a surfactant are dispersed in a solvent, (b) adding an active material to the coating liquid such that the conductive agent is coated onto the surface of the active material, and (c) heat-treating the coated active material.

According to another aspect of the present invention, the active material is prepared through the steps of: (a) preparing a coating liquid where a conductive agent and a dispersant are dispersed in a solvent, (b) adding an active material to a surfactant-containing solution, and thoroughly mixing the solution, (c) mixing the coating liquid made at the (a) step with the active material-containing solution made at the (b) step such that the conductive agent is coated onto the surface of the active material, and (d) heat-treating the coated active material.

According to still another aspect of the present invention, the active material is prepared through the steps of: (a) preparing a coating liquid where a conductive agent and a conductive polymeric dispersant are dispersed in a

solvent, (b) adding an active material to the coating liquid, (c) coating the conductive agent and the conductive polymeric dispersant onto the surface of the active material, and (d) heat-treating the coated active material.

An electrode comprising the coated active material may be fabricated through the steps of: (a) preparing a binder-containing solution where a binder is dissolved in a solvent, (b) adding the coated active material to the binder-containing solution to thereby prepare a slurry, and (c) coating the slurry onto a current collector and pressing it to thereby form an electrode.

Alternatively, the electrode may be fabricated through the steps of: (a) preparing a coating liquid where a conductive agent, a conductive polymeric dispersant and a binder are dispersed in a solvent, (b) adding an active material to the coating liquid to thereby prepare a slurry where the conductive agent and the conductive polymeric dispersant are coated onto the surface of the active material, and (c) coating the slurry onto a current collector and pressing it to thereby form an electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings in which like reference symbols indicate the same or the similar components, wherein:

Fig. 1A illustrates the diffusion degree of a conductive agent in the presence of a dispersant;

Fig. 1B illustrates the diffusion degree of a conductive agent in the absence of the dispersant;

Fig. 2 illustrates the diffusion state of an active material with the addition of a surfactant;

Fig. 3A illustrates the steps of fabricating an electrode using an active material according to a prior art;

Fig. 3B illustrates the steps of fabricating an electrode using an active material according to a preferred embodiment of the present invention;

Fig. 3C illustrates the steps of fabricating an electrode using an active material according to another preferred embodiment of the present invention;

Fig. 4 illustrates the combination state of a conductive polymeric dispersant and N-methyl pyrrolidone existent on the surface of an active material;

Figs. 5A and 5B are Scanning Electron Microscopy (SEM) photographs of a positive active material powder according to Comparative Example1;

Figs. 6A and 6B are SEM photographs of a positive active material powder according to Example 1;

Figs 7A and 7B are SEM photographs of an electrode according to Comparative Example 1;

Figs. 8A and 8B are SEM photographs of an electrode according to Example 1;

Figs. 9A and 9B are SEM photographs of an electrode according to Example 2;

Fig. 10 is a graph illustrating the charge and discharge curves of a half-

cell according to Comparative Example 1;

Fig. 11 is a graph illustrating the discharge capacity characteristic of a half-cell according to Example 1;

Fig. 12 is a graph illustrating the discharge capacity characteristic of a lithium ion battery cell with a positive active material according to Comparative Example 1;

Fig. 13 is a graph illustrating the discharge capacity characteristic of a lithium ion battery cell with a positive active material according to Example 1;

Fig. 14 is a graph illustrating the discharge capacity characteristic of a lithium ion battery cell with a positive active material according to Example 4; and

Fig. 15 is a graph illustrating the cycle life characteristic of lithium ion battery cells with a positive active material according to Example 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of this invention will be explained in detail.

According to the present invention, the conductive agent to be conventionally added to a slurry for fabricating an electrode is directly coated onto an active material. That is, the active material is overlaid with a coating layer comprising a conductive agent, or a mixture of a conductive agent and a conductive polymeric dispersant.

Conventionally, the active material and the conductive agent are mixed in the slurry for electrode fabrication. However, in the present invention, the conductive agent is directly coated onto the active material so that the amount

of the conductive agent required for the electrode fabrication can be decreased. Consequently, the addition reaction of the conductive agent with the electrolyte is reduced while decreasing the occurrence of gas in the battery cell. This prohibits swelling of the battery cell while securing safety thereof.

Any material capable of electrochemically undergoing the oxidation-reduction reactions can be used for the active material. The electrochemically oxidizable and reducible material includes a metal, a lithium-containing alloy, sulfur-based compounds, compounds that can reversibly form lithium-containing compounds by a reaction with lithium ions, and all materials that can reversibly intercalate/deintercalate lithium ions (lithiated intercalation compounds), although the present invention is not limited thereto.

The metal includes lithium, tin or titanium. The lithium-containing alloy includes a lithium/aluminum alloy, a lithium/tin alloy, or a lithium/magnesium alloy. The sulfur-based compounds, which form the positive active material of the lithium-sulfur battery, include a sulfur element, Li_2S_n ($n \geq 1$), an organic sulfur compound and a carbon-sulfur polymer ($(C_2S_x)_n$ where $x= 2.5$ to 50 and $n \geq 2$). The compound that can reversibly form a lithium-containing compound by a reaction with lithium ions includes silicon, titanium nitrate or tin oxide.

The active materials that can reversibly intercalate/deintercalate lithium ions (lithiated intercalation compounds) include carbon-based materials, lithium-containing metal oxides, and lithium-containing chalcogenide compounds. The carbon-based material can be non-crystalline carbon, crystalline carbon, or a mixture thereof. Examples of the non-crystalline carbon include soft carbon (low-temperature calcinated carbon), and hard carbon (high-temperature

calcinated carbon). Examples of crystalline carbon include natural graphite or artificial graphite which are of a plate, sphere or fiber shape.

The lithium-containing metal oxide and lithium-containing chalcogenide compound has a monoclinic, hexagonal or cubic structure as a basic structure.

A conventional lithium-containing compound (lithium-containing metal oxide and lithium-containing chalcogenide compound) can be used as the lithiated intercalation compound of the present invention, and preferable examples are compounds having the following formulas (1) to (13):

$Li_xMn_{1-y}M'_yA_2$ (1)

$Li_xMn_{1-y}M'_yO_{2-z}A_z$ (2)

$Li_xMn_2O_{4-z}A_z$ (3)

$Li_xMn_{2-y}M'_yA_4$ (4)

$Li_xCo_{1-y}M'_yA_2$ (5)

$Li_xCoO_{2-z}A_z$ (6)

$Li_xNi_{1-y}M'_yA_2$ (7)

$Li_xNiO_{2-z}A_z$ (8)

$Li_xNi_{1-y}Co_yO_{2-z}A_z$ (9)

$Li_xNi_{1-y-z}Co_yM'_zA_\alpha$ (10)

$Li_xNi_{1-y-z}Co_yM'_{zy}O_{2-\alpha}A_\alpha$ (11)

$Li_xNi_{1-y-z}Mn_yM'_zA_\alpha$ (12)

$Li_xNi_{1-y-z}Mn_yM'_zO_{2-\alpha}A_\alpha$ (13)

wherein $0.95 \leq x \leq 1.1$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, $0 < \alpha \leq 2$;

M' is at least one element selected from the group consisting of Al, Ni,

Co, Mn, Cr, Fe, Mg, Sr, V, and a rare-earth element; and

A is at least one element selected from the group consisting of O, F, S and P.

The average diameter of the lithium-containing compound is preferably in the range of 1 to 50 μm, more preferably in the range of 5 to 20 μm, and most preferably in the range of 5 to 10 μm.

The coating layer formed on the surface of the active material contains a conductive agent, or a mixture of a conductive agent and a conductive polymeric dispersant.

The conductive agent may be selected from a carbon-based conductive agent, a graphite-based conductive agent, a metal-based conductive agent or a metallic compound-based conductive agent, but it is not limited thereto.

KS6 (produced by the Timcal company) may be used as the graphite-based conductive agent. The carbon-based conductive agent may be selected from Super P (produced by the MMM company), ketchen black, denka black, acetylene black, carbon black, thermal black, or channel black. The metal or metallic compound-based conductive agent may be selected from tin, tin oxide, or tin phosphate ($SnPO_4$).

The amount of the conductive agent in the coating layer is preferably in the range of 0.1 to 10 wt% of the active material, and more preferably in the range of 1 to 4 wt%. In the case the amount of the conductive agent is less than 0.1 wt%, the electrochemical characteristics of the active material become deteriorated. By contrast, in the case the amount of the conductive agent is more than 10 wt%, the energy density per weight of the active material is

decreased.

It is preferable that the average particle diameter of the conductive agent in the coating layer is 1 ㎛ or less. In such a diameter range, the conductive agent is well attached to the surface of the active material. By contrast, the conductive agent cannot be well attached to the active material in the diameter range of more than 1 ㎛.

According to a first preferred embodiment of the present invention, the coated active material can be prepared through the steps of: (a) preparing a coating liquid where a conductive agent, a dispersant and a surfactant are dispersed in a solvent, (b) adding an active material to the coating liquid to thereby coat the conductive agent onto the surface of the active material, and (c) heat-treating the coated active material.

According to a second preferred embodiment of the present invention, the coated active material can be prepared through the steps of: (a) preparing a coating liquid where a conductive agent and a dispersant are dispersed in a solvent, (b) adding an active material to a surfactant-containing solution to make an active material-containing solution, (c) mixing the coating liquid made at the (a) step with the active material-containing solution made at the (b) step to thereby coat the conductive agent onto the surface of the active material, and d) heat-treating the coated active material.

The dispersant for dispersing the conductive agent may be selected from a polyacrylate-based resin; polyethylene oxide; a block copolymer of $(EO)_l(PO)_m(EO)_l$ where EO indicates ethylene oxide, PO indicates propylene oxide, and l and m are in the numerical range of 1 to 500; polyvinyl chloride

(PVC); an acrylonitrile/butadiene/styrene (ABS) polymer; an acrylonitrile/styrene/acrylester (ASA) polymer; a mixture of the ABS polymer and propylene carbonate; a styrene/acrylonitrile (SAN) copolymer; or a methylmethacrylate/acrylonitrile/butadiene/styrene (MABS) polymer. A resin of Orotan™ may be used for the polyacrylate-based resin.

The amount of the dispersant is preferably in the range of 0.1 to 20 wt% of the conductive agent. The diffusion state of the conductive agent (Super P) in a solvent of N-methyl pyrrolidone with or without the dispersant in the N-methyl pyrrolidone solvent is illustrated in Figs. 1A and 1B. As shown in Fig. 1A, the conductive agent is uniformly dispersed in the presence of the dispersant. By contrast, as shown in Fig. 1B, the conductive agent is not uniformly distributed in the absence of the dispersant, but conglomerated sporadically.

The surfactant works as a binder for binding the conductive agent to the active material. Non-ionic, anionic and cationic materials as well as organic or inorganic materials may all be used as the surfactant. The surfactant includes a hydrophilic head group and a hydrophobic tail group in its respective molecules. The hydrophilic head group includes an ionic group and a non-ionic group. The ionic group makes static-electricity bonding, and the non-ionic group makes hydrogen bonding.

For instance, the compounds having the ionic group include sulfonate (RSO_3^-), sulfate (RSO_4^-), carboxylate ($RCOO^-$), phosphate (RPO_4^-), ammonium ($R_xH_yN^+$: x is in the numerical range of 1 to 3, and y is in the numerical range of 3 to 1), quaternary ammonium (R_4N^+), betaines ($RN^+(CH_3)_2CH_2COO^-$), and

sulfobetaines ($RN^+(CH_3)_2CH_2SO_3^-$). The compounds having the non-ionic group include polyethylene oxide ($R\text{-}OCH_2CH_2(OCH_2CH_2)_nOH$), amine compounds, and gelatins. In the above compounds, R indicates the saturated or non-saturated hydrogen carbide where the number of carbons is preferably in the range of 2 to 1000. The surfactant bears a molecular weight preferably in the range of 5 to 10,000, more preferably in the range of 50 to 5000, and most preferably in the range of 50 to 300.

The active material bears a hydrophobic property. Therefore, when the active material is dispersed in a solvent together with the surfactant, as shown in Fig. 2, the molecules of the active material are separated from each other, and dispersed.

The amount of the surfactant is preferably 0.1 to 20 wt% of the conductive agent. Within this range, the amount of the conductive agent to be coated onto the active material can be controlled in a desired manner.

In the case of a surfactant with both anions and cations, the pH of the coating liquid affects the amount of the conductive agent to be coated onto the active material. When betaines, sulfobetaines or gelatins are used as the surfactant, it is preferable that in the coating process according to the second preferred embodiment the pH of the surfactant-containing solution to be used at the (b) step is kept to be 3 to 4, and the pH of the conductive agent-containing solution at the (c) step is kept to be 5 to 8, and more preferably to be 6 to 7.

The method of preparing such a coated active material using gelatin includes the steps of: (a) preparing a coating liquid where a conductive agent and a dispersant are dispersed in a solvent, (b) preparing a gelatin-containing

solution where gelatin is dissolved in a solvent and adding an acid to the gelatin-containing solution while controlling the pH thereof to be 3 to 4, c) adding an active material to a gelatin-containing solution followed by agitating, d) removing the gelatin residue from the surface of the active material to obtain an active material-containing solution while controlling the pH of the active material-containing solution to be 5 to 8, e) mixing the coating liquid made at the (a) step with the active material-containing solution made at the (d) step to thereby coat the conductive agent onto the surface of the active material, and e) heat-treating the coated active material. The pH is controlled with the addition of an acid or base such as acetic acid, hydrochloric acid, sulfuric acid, or ammonia.

The solvent may be selected from water, organic solvent, or a mixture thereof. The organic solvent may be selected from alcohols such as methanol, ethanol and isopropanol, hexane, chloroform, tetrahydrofuran, ether, methylene chloride, acetone, acetonitrile, or N-methyl pyrrolidone (NMP). In the case the surfactant is a compound bearing an ionic group, an organic solvent is preferably used for the solvent. In the case the surfactant is a compound bearing a non-ionic group, water is preferably used for the solvent.

The coating of the active material is preferably made by way of a wet coating technique such as spray coating, or impregnation dip coating.

In the above process, the heat treatment is preferably done at 100 to 500℃, and the period of time for the heat treatment is preferably in the range of 1 to 20 hours. The surfactant, and the dispersant used for dispersing the conductive agent are removed during the heat treatment process. In the case

the heat treatment temperature is less than 100℃, the surfactant residue is present at the surface of the active material while making bad effects to the electrochemical characteristics thereof. In the case the heat treatment temperature is over 500℃, the amount of the conductive agent is undesirably decreased.

Under the application of a conductive polymeric dispersant, the coated active material can be easily prepared compared to the case where the usual surfactant is used.

In a third preferred embodiment of the present invention, the active material coated with a mixture of a conductive polymeric dispersant and a conductive agent is prepared through the steps of: (a) preparing a coating liquid where a conductive agent and a conductive polymeric dispersant are dispersed in a solvent, (b) adding an active material to the coating liquid, (c) coating the conductive agent and the conductive polymeric dispersant onto the active material, and (d) heat-treating the coated active material.

In the case a conductive polymeric dispersant is used as the surfactant, the conductive agent and the conductive polymeric dispersant are coexistent at the coating layer of the active material. That is, the conductive polymeric dispersant is existent on the surface of the active material while being differentiated from a usual surfactant. As with the conductive agent, the conductive polymeric dispersant forms a conductive network to thereby improve the electrochemical characteristics of the active material. The conductive polymeric dispersant has a role of dispersing the conductive agent, and also functions as a surfactant for attaching the conductive agent to the active

material.

The conductive polymeric dispersant may be selected from polyethylene oxide; polypropylene oxide; a block copolymer of $(EO)_l(PO)_m(EO)_l$ where EO indicates ethylene oxide, PO indicates propylene oxide, and l and m are in the numerical range of 1 to 500; polyvinylidene chloride (PVC); an acrylonitrile/butadiene/styrene (ABS) polymer; an acrylonitrile/styrene/acrylester (ASA) polymer; a mixture of the ABS polymer and propylene carbonate; a styrene/acrylonitrile (SAN) copolymer; or a methylmethacrylate/acrylonitrile/butadiene/styrene (MABS) polymer. Among them, the $(EO)_l(PO)_m(EO)_l$ is the best candidate for the conductive polymeric dispersant.

In the $(EO)_l(PO)_m(EO)_l$ block copolymer, propylene oxide bears a hydrophobic property, and hence is attached to the active material or the conductive agent. Ethylene oxide bears a hydrophilic property and conductivity, and hence has a role of interconnecting the active material and the conductive agent while conducting the lithium ions. The currently available conductive polymeric dispersant may be selected from P-series in a cake state (produced by the BASF company), or F-series in a powder state (produced by the BASF company).

The conductive agent frequently employed for use in the conductive agent coating process with a usual surfactant can be directly used for the present conductive agent. It is preferable that the amount of the conductive polymeric dispersant is 0.1 to 20 wt% of the conductive agent.

The solvent suitable for the conductive polymeric dispersant may be

selected from alcohols such as methanol, ethanol and isopropanol, hexane, chloroform, tetrahydrofuran, ether, methylene chloride, acetone, acetonitrile, or N-methyl pyrrolidone (NMP).

Since there is no need to remove the conductive polymeric dispersant, the heat treatment temperature may be established to be 100℃ or less.

The coating of the active material is preferably made by way of a usual wet coating technique such as spray coating, and impregnation dip coating.

A coating layer based on MPO_4, MSO_4 or MWO_4, where M is a group 3B element, may be formed on the active material using a surfactant to improve the stability and electrochemical characteristics of the active material. For instance, an active material with a coating layer of MPO_4 may be prepared through the steps of: (a) adding an active material and a phosphate-based surfactant to an alcohol-based solvent, b) adding a compound of MX_3,where M is a group 3B element and X is a halogen element, to the active material-containing solution such that M^{3+} ions form static electricity bonding with the hydrophilic head group of the surfactant, and c) filtering the active material with the static electricity bonding, and baking it at low temperature to thereby form a mesoporous MPO_4 coating layer on the surface of the active material. When a sulfate-based surfactant is used instead of a phosphate-based surfactant, an MSO_4 coating layer is formed on the surface of the active material.

The coating layer comprising the conductive agent or the mixture of the conductive agent and the conductive polymeric dispersant reduces the internal resistance of the active material while preventing the discharge potential thereof from being deteriorated. Accordingly, a high discharge potential can be

maintained in a constant manner irrespective of variation in the current density (C-rate). This is because the conductive agent coated on the surface of the active material reduces the surface polarization. Accordingly, in the case the surface-treated active material is applied for practical use in the battery cell, the performance characteristics of the battery cell such as cycle life, discharge potential and power density can be improved.

When the active material coated with a conductive agent is used in the battery cell fabrication, the density of the electrode active material is enhanced so that the energy density of the resulting battery cell is heightened in a significant manner. Particularly, it can largely serve to make prismatic battery cells bear a slim size while involving a high capacity.

In order to be marketable, batteries should pass various stability tests. The penetration test in which a nail is passed through a charged battery cell, is critical for guaranteeing the stability of the battery. The stability of the battery depends on various factors, especially exothermic reaction caused by reacting the charged positive electrode with electrolyte immersed in the charged positive electrode.

For instance, when a coin cell including an active material of $LiCoO_2$ is charged by a predetermined electric potential, $LiCoO_2$ is converted to $Li_{1-x}CoO_2$. The thermal stability of the active material can be judged based on the exothermic starting temperature and exothermic heat amount, from the measurement of differential scanning calorimetry (DSC) with respect to the charged material. The active material of $Li_{1-x}CoO_2$ is unstable in its charged state. Accordingly, the internal temperature of the battery cell is heightened so

that the oxygen content is separated from the cobalt content. The separated oxygen content reacts with the electrolyte, and this can cause an possible explosion of the battery cell. Therefore, the oxygen releasing temperature (the exothermic starting temperature) and the exothermic heat amount are important factors in representing the stability of the battery cell. The inventive active material involves significantly reduced exothermic heat, and this insures thermal stability of the resulting battery cell.

A high-density electrode can be fabricated using the active material where a surface-treatment layer is present and also comprises a coating compound and a conductive agent. The electrode is fabricated through the steps of: (a) preparing a binder-containing solution where a binder is dissolved in a solvent, b) adding the active material to the binder-containing solution to prepare a slurry, and c) coating the slurry onto a current collector and pressing it to thereby form an electrode.

The conventional electrode fabrication process and the inventive electrode fabrication process are illustrated in Figs. 3A to 3C. As shown in Fig. 3A, in the conventional process, an active material and a conductive agent are put to a binder-containing solution to prepare a slurry, and the slurry is coated onto a current collector followed by pressing to thereby form an electrode. By contrast, as shown in Fig. 3B, in the inventive process, the conductive agent is not added to the active material in preparing the slurry. That is, the active material with a conductive agent-based coating layer is added to a binder-containing solution to prepare a slurry, and the slurry is coated onto a current collector and is pressed to thereby form an electrode. In the inventive

electrode, the conductive agent is distributed through the active material more uniformly than in the conventional electrode using uncoated active material. Furthermore, under the application of a conductive polymeric dispersant, as shown in Fig. 3C, the active material coating process can be made during the process of preparing the slurry so that the overall processing steps can be simplified.

Meanwhile, in the electrode fabrication process using the coated active material, the amount of the conductive agent can be reduced without influencing the electrochemical characteristics of the battery cell. Consequently, the addition reaction of the conductive agent with the electrolyte is reduced while decreasing the occurrence of gas in the battery cell. This prohibits swelling of the battery cell while securing safety thereof.

Furthermore, the amount of the binder for reinforcing the binding of the conductive agent to the active material can be reduced together with that of the organic solvent such as N-methyl pyrrolidone for the slurry, decreasing the production cost. The amount of the active material is increased by the amount of reduction of the conductive agent and the binder, resulting in enhanced electrode density. Accordingly, when the inventive active material is employed for use in fabricating a battery cell, the stability of the cell can be improved while maintaining the electrochemical characteristics thereof.

The coated active material bears excellent adhesive strength with respect to the electrode, and hence the resulting battery cell does not suffer an increase in the internal resistance thereof due to possible detachment of the active material during cycling. Accordingly, in the case the electrode is

fabricated using the coated active material, suitable adhesive strength can be obtained even with a reduction in the amount of binder.

In the case a conductive polymeric dispersant is used as the surfactant, the active material coated with the mixture of the conductive agent and the conductive polymeric dispersant is added to a binder-containing solution to prepare a slurry. It is also possible that the binder, the conductive agent and the conductive polymeric dispersant are mixed together, and a non-coated active material is added to the mixture to thereby prepare a slurry. In the latter case, as shown in Fig. 3C, the process of coating the conductive agent and the conducting high molecule dispersant onto the active material, and the process of preparing the slurry may be made through one process.

The process of fabricating an electrode using a conductive polymeric dispersant is made through the steps of: (a) preparing a coating liquid where a conductive agent, a conductive polymeric dispersant and a binder are dispersed in a solvent, (b) adding an active material to the coating liquid to prepare a slurry, and (c) coating the slurry onto a current collector and pressing it to thereby form an electrode.

The conductive polymeric dispersant has a property of being well dissolved in the solvent for the electrode fabrication, and further has a role of making the binder be well dissolved in the slurry. It is preferable that the amount of the conductive agent is 0.5 to 5 wt% of the active material, the amount of the conductive polymeric dispersant is 0.1 to 20 wt% of the conductive agent, and the amount of the binder is 0.5 to 20 wt% of the active material.

The following examples further illustrate the present invention.

Comparative Example 1

Polyvinylidene fluoride for a binder was added to N-methyl pyrrolidone to thereby prepare a binder-containing solution. A powder of $LiCoO_2$ with an average particle diameter of 10 μm for a positive active material, and Super P for a conductive agent were added to the binder-containing solution, and it was mixed for 4 hours. The mixture was then aged for 4 hours to thereby form a slurry. The weight ratio of the positive active material, the conductive agent and the binder was established to be 94/3/3. The slurry was coated onto an Al-foil to a thickness of about 100 μm and pressed with a pressure of 1 ton to thereby fabricate a positive electrode for a coin cell. The positive electrode was punched to bear a hole with a diameter of 1.6 cm. A coin-type half-cell was fabricated by using this positive electrode and lithium metal as a counter electrode in a glove box. For the electrolyte, 1M $LiPF_6$ solution of mixed solvent of ethylene carbonate and dimethyl carbonate in the volume ratio of 1:1 was used.

Comparative Example 2

A coin-type half-cell was fabricated in the same way as with Comparative Example 1 except that a powder of $LiMn_2O_4$ having an average particle diameter of 15 μm was used for the positive active material.

Comparative Example 3

A coin-type half-cell was fabricated in the same way as with Comparative Example 1 except that a powder of $LiNi_{0.9}Sr_{0.002}Co_{0.1}O_2$ having an

average particle diameter of 10 μm was used for the positive active material.

Comparative Example 4

A coin-type half-cell was fabricated in the same way as with Comparative Example 1 except that a powder of $LiNi_{0.66}Mn_{0.25}Al_{0.05}Mg_{0.05}Co_{0.1}O_2$ having an average particle diameter of 10 μm was used for the positive active material.

Comparative Example 5

A coin-type half-cell was fabricated in the same way as with Comparative Example 1 except that the weight ratio of the positive active material, the conductive agent and the binder was established to be 96/2/2.

Example 1

100 mℓ of water, a 500g zirconia ball, 3g of Super P for a conductive agent, and 0.5g of Orotan™ (produced by the Hanchung Chem company) were poured into a 300 mℓ plastic bottle, and ball-milled for 2 hours to thereby prepare a solution where the Super P was completely dispersed.

A solution where 1g of gelatin was dissolved in 200 mℓ of water was thoroughly mixed, and 100g of $LiCoO_2$ with an average particle diameter of 10 μm was added to the solution. The pH of the solution was controlled to be 3 to 4 with the addition of acetic acid. Then, the solution was filtered such that the gelatin not coated on the active material could be removed. Water was again added to the filtered solution while controlling the pH thereof to be 5 to 8. The solution with the completely dispersed Super P was mixed with the pH-controlled solution, and the mixed solution was thoroughly mixed for 5 minutes.

Under such a pH condition, the $-COO^{-}$ group in the gelatin makes hydrogen bonding with the -OH group in the Super P. After mixing, the Super P-coated $LiCoO_2$ was settled down such that it could be easily recovered. The solution was dried at 130℃, and baked at 300℃ for 10 minutes so that the gelatin content was completely removed from the $LiCoO_2$. As a result, a powder of $LiCoO_2$ coated with 0.5 wt% of Super P is coated was produced. A binder-containing solution was prepared through mixing polyvinylidene fluoride for a binder with N-methyl pyrrolidone (NMP), and the $LiCoO_2$ powder was added to the binder-containing solution to thereby prepare a slurry. The weight ratio of the active material to the binder was established to be 99/1, and the Super P was not added thereto. The slurry was coated onto an Al-foil to a thickness of about 200 ㎛ and pressed with a pressure of 1 ton to thereby fabricate a positive electrode for a coin cell. The positive electrode was punched to bear a hole with a diameter of 1.6 ㎝. A coin-type half-cell was fabricated by using this positive electrode and lithium metal as a counter electrode in a glove box. For the electrolyte, 1M $LiPF_6$ solution of mixed solvent of ethylene carbonate and dimethyl carbonate in the volume ratio of 1:1 was used.

In the case the slurry was prepared using the positive active material of Comparative Example 1, the time period for mixing the slurry reached 4 or more hours because the diffusion of the active material and the conductive agent was not easily made. By contrast, in the case the slurry was prepared using the positive active material of Example 1, the time period for mixing the slurry was significantly reduced while the diffusion of the active material and the

conductive agent was made in a uniform manner. The time period for fabricating the electrode becomes shortened while enhancing the cell production efficiency.

Example 2

A coin-type half-cell was fabricated in the same way as with Example 1 except that the amount of gelatin was 2g.

Example 3

A coin-type half-cell was fabricated in the same way as with Example 1 except that the amount of gelatin was 3g.

Example 4

A block copolymer of $(EO)_l(PO)_m(EO)_l$ (pluronic series™ of the BASF company), and Super P were put into N-methyl pyrrolidone, and ball-milled for 6 hours. Polyvinylidene fluoride was added to the mixture, and $LiCoO_2$ with an average particle diameter of 10 ㎛ was added thereto as an active material to thereby prepare a slurry. The oxygen content of the group of EO in the block copolymer was well bonded to the positive (+) charge of the N-methyl pyrrolidone attached to the active material. For this reason, the Super P attached to the PO group is well coated onto the surface of the $LiCoO_2$. This process is schematically illustrated in Fig. 4. The weight ratio of the active material, the Super P and the polyvinylidene fluoride in the slurry was established to be 97:1:2. The amount of the block copolymer of $(EO)_l(PO)_m(EO)_l$ was 50 wt% of the Super P. The slurry was coated onto an Al-based foil to a thickness of about 200 ㎛ and pressed with a pressure of 1 ton to thereby fabricate a positive electrode for a coin cell. The positive

electrode was punched to bear a hole with a diameter of 1.6 cm. A coin-type half-cell was fabricated by using this positive electrode and lithium metal as a counter electrode in a glove box. For the electrolyte, 1M $LiPF_6$ solution of mixed solvent of ethylene carbonate and dimethyl carbonate in the volume ratio of 1:1 was used.

Example 5

A coin-type half-cell was fabricated in the same way as with Example 1 except that a powder of $LiMn_2O_4$ with the average particle diameter of 15 μm was used instead of the powder of $LiCoO_2$.

Example 6

A coin-type half-cell was fabricated in the same way as with Example 4 except that a powder of $LiMn_2O_4$ with an average particle diameter of 15 μm was used instead of the powder of $LiCoO_2$.

Example 7

A coin-type half-cell was fabricated in the same way as with Example 1 except that a powder of $LiNi_{0.9}Sr_{0.002}Co_{0.1}O_2$ with an average particle diameter of 10 μm was used instead of the powder of $LiCoO_2$.

Example 8

A coin-type half-cell was fabricated in the same way as with Example 4 except that a powder of $LiNi_{0.9}Sr_{0.002}Co_{0.1}O_2$ with an average particle diameter of 10 μm was used instead of the powder of $LiCoO_2$.

Example 9

A coin-type half-cell was fabricated in the same way as with Example 1

except that a powder of $LiNi_{0.66}Mn_{0.25}Al_{0.05}Mg_{0.05}Co_{0.1}O_2$ with an average particle diameter of 10 μm was used instead of the powder of $LiCoO_2$.

Example 10

A coin-type half-cell was fabricated in the same way as with Example 4 except that a powder of $LiNi_{0.66}Mn_{0.25}Al_{0.05}Mg_{0.05}Co_{0.1}O_2$ with an average particle diameter of 10 μm was used instead of the powder of $LiCoO_2$.

Example 11

A coin-type half-cell was fabricated in the same way as with Example 1 except that tin oxide (SnO_2) was used for the active material.

Example 12

A coin-type half-cell was fabricated in the same way as with Example 4 except that SnO_2 was used for the active material.

Example 13

A coin-type half-cell was fabricated in the same way as with Example 1 except that silicon (Si) was used for the active material.

Example 14

A coin-type half-cell was fabricated in the same way as with Example 4 except that silicon (Si) was used for the active material.

Example 15

10g of a graphite powder and 0.1g of phosphoric acid ester (degressal™ SD40 produced by the BASF company) were added to alcohol. As the graphite powder bears a hydrophobic property, the hydrophobic groups in the phosphate were bonded thereto. $AlCl_3$ was added to the solution such that Al_3^+ ions could be bonded to the hydrophilic head groups of the phosphate

by way of static electricity bonding. The resulting solution was filtered, and baked at 300℃ to thereby obtain a graphite powder where mesoporous $AlPO_4$ was uniformly coated on the surface thereof. A coin-type half-cell was fabricated using the graphite powder.

Figs. 5A and 5B are SEM photographs of the non-coated $LiCoO_2$ powder according to Comparative Example 1. Figs. 6A and 6B are SEM photographs of the $LiCoO_2$ powder coated with the Super P-based conductive agent according to Example 1. It can be verified from the photographs that the powder according to Example 1 has a surface shape entirely different from that according to Comparative Example 1.

Figs. 7A, 8A and 9A are SEM photographs of the electrodes according to Comparative Example 1, and Examples 1 and 2, and Figs. 7B, 8B and 9B are amplified photographs of those electrodes. In the electrode according to Comparative Example 1, it can be observed from the SEM photograph of Fig. 7A that the Super P is not existent on the active material, but it fills the empty portions of the electrode in a separate manner. However, in the electrodes according to Examples 1 and 2, it can be noticed from the SEM photographs of Figs. 8A and 9A that the Super P is coated on the active material while being distributed in a uniform manner.

The amount of conductive agent in the electrodes according to Examples 1 to 3 (based on the electrode) and Comparative Example 1 and the density of the active material therein were computed, and the results are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1
Amount of conductive agent (wt%)	0.15	0.3	0.5	3
Density of active material (mg/㎠)	47	44	42	32

The density of the active material in the electrodes according to Examples 1 to 3 was increased by 30 to 40% compared to that according to Comparative Example 1. Therefore, it can be predicted that the density of the electrode would be also increased by 30 to 40%.

The coin-type half-cell according to Comparative Example 1 was charged and discharged at 0.2C, 0.5C and 1C rates in the voltage range of 2.75 to 4.3V, and the results are illustrated in Fig. 10. It can be observed from Fig. 10 that the cell capacity at the 1C rate is radically deteriorated. Likewise, the cell according to Example 1 was charged and discharged, and the discharge characteristics thereof are illustrated in Fig. 11. It can be observed from the drawing that the discharge potential of the cell at the 1C rate is approximated to that at the 0.2C rate. Furthermore, the discharge capacity at the 1C rate after the 40 cycling was decreased at most by 1% compared to the initial discharge capacity.

Prismatic lithium ion cells including the positive active materials of Examples and Comparative Examples were fabricated, and the capacity characteristics thereof pursuant to C-rates were measured. The lithium ion cell was fabricated in the following way. A positive active material, and

polyvinylidene fluoride for a binder were mixed in the weight ratio of 98/2 to thereby prepare a slurry. The slurry was coated onto an Al-foil and pressed to thereby fabricate a positive electrode. Synthetic graphite for a negative active material and polyvinylidene fluoride for a binder were mixed in the weight ratio of 90/10 to thereby prepare a slurry. The slurry was coated onto a Cu-foil, and pressed to thereby fabricate a negative electrode. The negative and the positive electrodes were combined with each other, and an electrolyte was injected between them to thereby fabricate a 700mAh prismatic lithium ion cell. For the electrolyte, 1M $LiPF_6$ solution of mixed solvent of ethylene carbonate and dimethyl carbonate in the volume ratio of 1:1 was used.

The capacity characteristics of the prismatic lithium ion cell including the positive active material of Comparative Example 1 pursuant to the C-rates were measured, and the results are illustrated in Fig. 12. It can be observed from the drawing that the discharge potential of the cell at the 2C rate is significantly reduced compared to that at the 1C rate. The capacity characteristics of the lithium ion cell including the positive active material of Example 1 pursuant to the C rates were measured, and the results are illustrated in Fig. 13. It can be observed from Fig. 13 that the battery cell exhibited 97% of the initial capacity even at the 2C rate. In the lithium ion cell including the positive active material of Example 4, the capacity characteristics thereof pursuant to the C-rates were measured, and the results are listed in Fig. 14. As shown in the drawing, the cell capacity exhibited 90% of the initial capacity even at the 2C rate. Furthermore, the discharge potential at the 2C rate was not reduced much as compared to that at the 1C rate. This is because the conductive agent is

coated on the surface of the active material while reducing the internal resistance thereof.

Two prismatic lithium ion cells were fabricated based on the positive active material of Example 1, and the cycle life characteristics thereof at the 1C rate were measured. The results are illustrated in Fig. 15. In the drawing, the diagonal line indicates the maintenance of the cycle life of 80%. It turned out that the cells after the 300 cycling proceed along the 80% cycle life maintenance line.

As described above, the inventive active material is coated with a conductive agent or a mixture of a conductive agent and a conductive polymeric dispersant, and hence involves improved capacity, cycle life, and safety. Furthermore, the active material bears a good adhesion characteristic to the electrode, so the resulting battery cell does not suffer an increase in internal resistance thereof due to detachment of the active material.

An electrode with the active material and the conductive agent uniformly distributed can be fabricated using the coated active material so that the electrochemical characteristics of the resulting battery cell can be improved.

The inventive active material preparation technique involves a reduced processing time compared to other techniques. Furthermore, in this technique, the amount of conductive agent, binder and slurry solvent can be reduced in a cost-effective manner while enhancing production efficiency.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the

spirit and scope of the present invention as set forth in the appended claims.